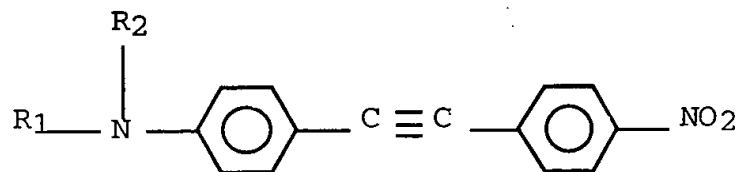
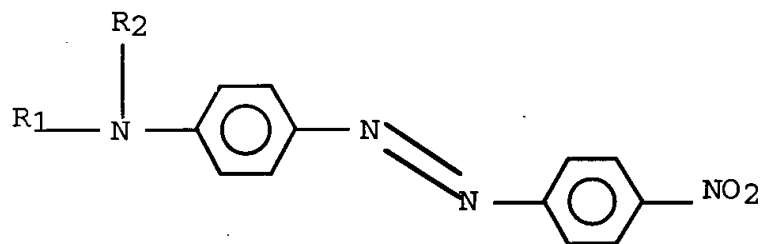


DOPANTS FOR LIQUID-CRYSTAL DEVICESBackground

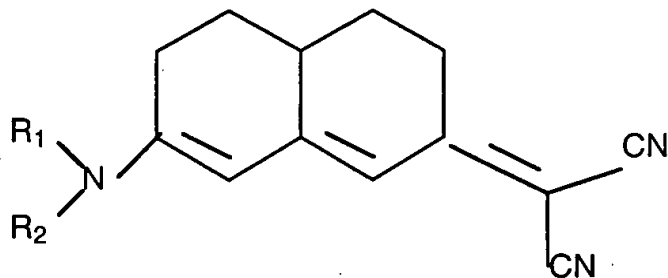
This invention concerns high-dielectric colorless or virtually colorless dopants for low-voltage and tunable clearing temperature liquid-crystal devices.

A few high dielectric anisotropy compounds have been reported in the literature.

For example, Wu et al., Asia Display, pp. 567-70 (1995) discloses nitro-amino azobenzenes and tolanses with the following structures:



In another example, Kippelen et al., Science 279, 54 (1998) discloses bicyano-amino polyene dyes with the following structure:



A general problem with the compounds and dyes disclosed by Wu et al. and Kippelen et al. is that their absorption is too large in the visible region. As a result, their light transmission is greatly reduced. This is particularly undesirable for some displays and electro-optic modulators where high transmittance is required.

Summary

The invention involves new colorless or virtually colorless dopant compounds that exhibit an extraordinarily large dielectric anisotropy, a reduced elastic constant, and relatively low viscosity when mixed with liquid crystals. Therefore, adding a few percent of such dopant compounds to a liquid-crystal mixture reduces its operation voltage significantly. The low-voltage operation enables a low-cost electronic driver to be used. In addition, the clearing temperature and birefringence of the mixture can be tuned by

simply adjusting the concentration of the dopants.

Brief Description of the Drawings

Figure 1 is a graph showing the voltage-dependent phase change of four E63™ LC cells that were studied.

Figure 2 is a graph showing the optical density of 1% the compound of formula I in a ZLI-2359™ LC mixture and the optical density of 1% the compound of formula IV in an ZLI-2359™ LC mixture.

Figure 3 is a graph showing dopant concentration-dependent clearing temperature (dots) and birefringence (squares) of an E7™ liquid-crystal mixture..

Description

The dopant compounds of the present invention are colorless or virtually colorless. That is, their absorption in the visible region is very small. (Typically, the absorption loss in the visible region or spectrum at room temperature (e.g., approximately 20-30°C or approximately 22°C) is greater than or equal to 0 (or about .01%) and less than or equal to about 5%; preferably, the absorption loss in the visible region is greater than or equal to 0 (or about .01%) and less than or equal to about 1%; more preferably, the absorption loss in the visible region is greater than or equal to 0 (or about .01%) and less than or equal to about .05%; even more preferably, the absorption loss in the visible region is greater than or equal to 0 and less than or equal to about .01%; and ideally the absorption loss in the visible region is close to 0.) Absorption loss is defined as the

percentage of the input light that is absorbed by the medium.

The dopant compounds of the present invention also possess a very large dielectric anisotropy at room temperature of approximately 20-30°C or approximately 22°C (e.g., greater than about 50; preferably greater than about 60; and more preferably greater than about 70) and a low viscosity at room temperature of approximately 20-30°C or approximately 22°C (e.g., lower than about 50 centi-poise; preferably lower than about 30 centi-poise; and more preferably lower than about 15 centi-poise).

These dopant compounds help reduce the operation voltage for both polar and non-polar liquid-crystal (LC) mixtures. In addition, the nematic range and birefringence of LC mixtures can be tuned by adjusting the concentration of the dopant compounds of the present invention. That is, these dopant compounds can be used to tune the clearing temperature of LC mixtures.

Thus, the invention includes a composition comprising one or more of the dopant compounds and a liquid-crystal mixture. (A liquid-crystal mixture may comprise or consist of only one liquid-crystal compound or may comprise or consist of two or more liquid-crystal compounds, wherein a liquid-crystal compound is a compound that exhibits a liquid-crystal phase. Examples of liquid-crystal mixtures include, but are not necessarily limited to, Merck's E7TM liquid-crystal mixture, Merck's E63TM liquid-crystal mixture, and Merck's ZLI-2359TM liquid-crystal mixture. The reason for mixing two or more LC compounds to yield an LC mixture is to widen the LC mixture's temperature range (i.e., the range from the melting point to the clearing point) because a single LC compound may not have a wide enough temperature range. The usually preferred

storage temperature for an LC device is from about -40°C to about 80°C. When two or more LC compounds are mixed in the proper concentration, the melting point of the resulting mixture may drop to the lowest available melting point.) The dopant compound or compounds may comprise any percentage of the composition. Thus, the dopant compound or compounds may comprise by weight about 99% or less of the composition; the dopant compound or compounds may comprise by weight about 75% or less of the composition; the dopant compound or compounds may comprise by weight about 50% or less of the composition; the dopant compound or compounds may comprise by weight about 25% or less of the composition; the dopant compound or compounds may comprise by weight about 15% or less of the composition; the dopant compound or compounds may comprise by weight about 10% or less of the composition; the dopant compound or compounds may comprise by weight about 5% or less of the composition; the dopant compound or compounds may comprise by weight about 3% or less of the composition; and the dopant compound or compounds may comprise by weight about 1% or less of the composition.

The composition described in the preceding paragraph preferably has at room temperature of approximately 20-30°C (or approximately 22°C) a relatively high $\partial n/\partial T$ (e.g., greater than about 0.005, or more preferably greater than about 0.01 or greater than about 0.05), wherein n is a refractive index of the composition at a visible wavelength (e.g., about 4000 Å to about 7000 Å or, more specifically, about 633 nm) and T is the temperature of the composition in °C. The $\partial n/\partial T$ represents the rate of refractive index change versus the temperature; and, thus, the unit measurement of $\partial n/\partial T$ in °C⁻¹. The larger the $\partial n/\partial T$, the lower the laser power needed for realizing the nonlinear refraction effect, which is desirable.

The invention includes a method for increasing a $\partial n/\partial T$ of a liquid-

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crystal mixture, the method comprising adding one or more of the dopant compounds to the liquid-crystal mixture to yield a resulting mixture. The invention also includes a method for reducing an operation voltage of a liquid-crystal mixture, the method comprising adding one or more of the dopant compounds to the liquid-crystal mixture to yield a resulting mixture. The invention includes a method for tuning a clearing temperature of a liquid-crystal mixture, the method comprising adding one or more of the dopant compounds to the liquid-crystal mixture to yield a resulting mixture. In addition, the invention includes a method for tuning birefringence of a liquid-crystal mixture, the method comprising adding one or more of the dopant compounds to the liquid-crystal mixture to yield a resulting mixture. The dopant compound or compounds may comprise any percentage of the resulting mixture. Thus, the dopant compound or compounds may comprise by weight about 99% or less of the resulting mixture; the dopant compound or compounds may comprise by weight about 75% or less of the resulting mixture; the dopant compound or compounds may comprise by weight about 50% or less of the resulting mixture; the dopant compound or compounds may comprise by weight about 25% or less of the resulting mixture; the dopant compound or compounds may comprise by weight about 15% or less of the resulting mixture; the dopant compound or compounds may comprise by weight about 10% or less of the resulting mixture; the dopant compound or compounds may comprise by weight about 5% or less of the resulting mixture; the dopant compound or compounds may comprise by weight about 3% or less of the resulting mixture; and the dopant compound or compounds may comprise by weight about 1% or less of the resulting mixture.

The low voltage operation of an LC device is highly desirable because it enables a low cost electronic driver to be used. Low threshold LC mixtures are particularly attractive for the cholesteric-LC display where the threshold voltage (V_{th}) increases

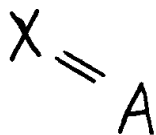
as the pitch length decreases. (D.L. White and G.N. Taylor, J. Appl. Phys. 45, 4718 (1974)) The recently developed polymer-stabilized cholesteric displays exhibit an excellent brightness and wide viewing angle. However, their operation voltage remain quite high ($\sim 50 V_{\text{rms}}$, wherein V_{rms} represents root-mean-square voltage). (D.K. Yang, et al., Appl. Phys. Lett. 64, 1905 (1994)) Consequently, there is an urgent need to reduce the operation voltage of these LC devices.

Based on the Freedericksz transition, the V_{th} of a homogeneously aligned LC cell is governed by the splay elastic constant (K_{11}) and dielectric anisotropy ($\Delta\epsilon$) of the LC material according to the formula: $V_{\text{th}} = \pi(K_{11}/\Delta\epsilon)^{1/2}$. A simple way to reduce V_{th} is to use high $\Delta\epsilon$ LC's, i.e., polar LC's with a large dipole moment, such as cyano group. Several cyano-biphenyl LC's (e.g., 4-cyano-4'-n-pentylbiphenyl (5CB)) do exhibit a large dielectric anisotropy ($\Delta\epsilon \sim 10$) and a relatively low melting point. These compounds have become the major components of many commercial LC mixtures, despite the fact that their clearing temperature (T_c) is not sufficiently high. To enhance the clearing point of LC mixtures, some high- T_c components are added. A general trend for the high- T_c LC compounds is that their melting point is also very high. For example, the melting-point temperatures (T_{mp}) of cyano-terphenyl (5CT) and cyano-diphenyl-diacetylene (PTTP-6CN) are 131°C and 145.3°C, respectively. A high melting point implies that the compound will have a poor solubility for forming eutectic mixtures.

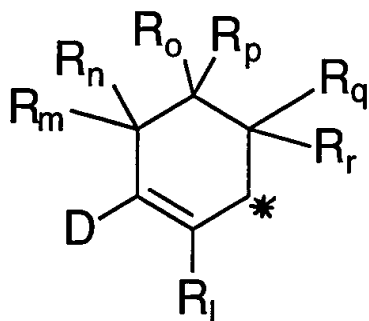
In this disclosure, we present some colorless (or virtually colorless), high-dielectric compounds for use as dopant materials for lowering the V_{th} of LC mixtures. Since these dopants possess a huge dielectric anisotropy, adding $\sim 3\%$ of such a dopant to an LC

mixture is enough to significantly reduce V_{th} while keeping viscosity low.

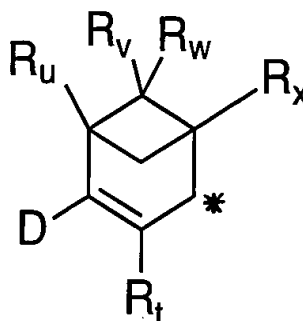
The invention comprises compounds illustrated below by the following formula A:



wherein X is selected from the group consisting of



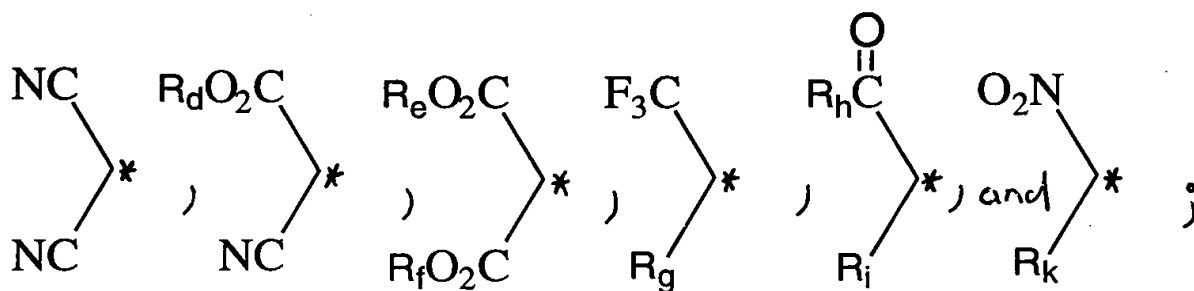
and



;

wherein D is selected from the group consisting of NR_aR_b , OR_a , SR_a , PR_aR_b , and R_c ;

wherein A is selected from the group consisting of:

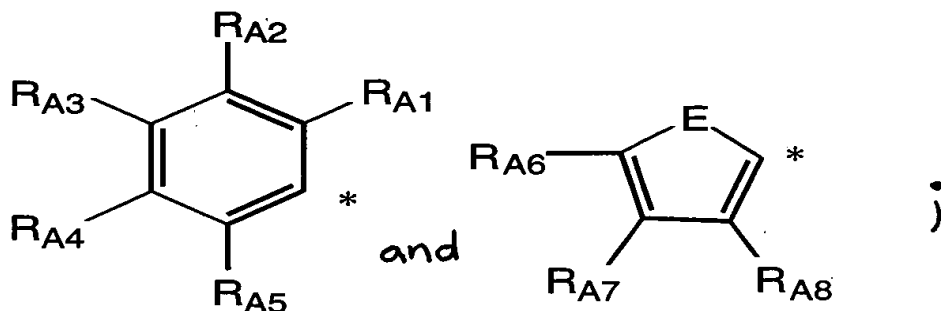


wherein R_a , R_b , and R_c are the same or different and are each independently selected from the group consisting of: H; a linear, branched, or cyclic alkyl group; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta OR_{A1}$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta NR_{A2}R_{A3}$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta CN$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta Cl$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta Br$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta I$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta$ -Phenyl; $-(CH_2)_\alpha(CF_2)_\gamma CF_3$; and an aryl group;

wherein R_d , R_e , R_f , R_l , R_m , R_n , R_o , R_p , R_q , R_r , R_s , R_t , R_u , R_v , R_w , and R_x are the same or different and are each independently selected from the group consisting of: H; a linear, branched, or cyclic hydrocarbon group that is saturated or unsaturated; a linear, branched, or cyclic alkyl group; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta OR_{A1}$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta NR_{A2}R_{A3}$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta CN$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta Cl$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta Br$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta I$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta$ -Phenyl; $-(CH_2)_\alpha(CF_2)_\gamma CF_3$; and an aryl group;

wherein R_g , R_h , R_i , and R_k are the same or different and are each independently selected from the group consisting of: H; a linear, branched, or cyclic hydrocarbon group that is saturated or unsaturated; a linear, branched, or cyclic alkyl group; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta OR_{A1}$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta NR_{A2}R_{A3}$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta CN$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta Cl$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta Br$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta I$; $-(CH_2CH_2O)_\alpha-(CH_2)_\beta$ -Phenyl; an aryl group; $-(CH_2)_\alpha(CF_2)_\gamma CF_3$; $-CO_2R_d$; and $-COR_d$;

wherein each aryl group is optionally independently selected from the group consisting of



wherein R_{A1} , R_{A2} , R_{A3} , R_{A4} , R_{A5} , R_{A6} , R_{A7} , and R_{A8} are the same or different and are each independently selected from the group consisting of H, a linear alkyl group, a branched alkyl group, and a cyclic alkyl group;

wherein E is selected from the group consisting of S, O, and NR_s ;

wherein the linear, branched, or cyclic hydrocarbon group that is saturated or unsaturated optionally includes up to 25 (or 8 or 5) carbon atoms (exemplary unsaturated hydrocarbons include, but are not necessarily limited to, ethylene, propylene, butene, methylpropene, pentene, hexene, methylbutene, ethyne, propyne, butyne, pentyne, hexyne, cyclopropene, cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclononene, cyclobutadiene, and cyclohexadiene; exemplary saturated hydrocarbons are set forth in the next paragraph);

wherein the linear, branched, or cyclic alkyl group optionally includes up to 25 (or 8 or 5) carbon atoms (exemplary alkyl groups include, but are not necessarily limited to, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, and nonyl, in the normal, secondary, iso, and neo attachment isomers; cyclopropane; cyclobutane; cyclopentane; cyclohexane; cycloheptane; cyclooctane; cyclononane; and decalin);

wherein α is an integer that is greater than or equal to 0 and less than or equal to 25 (or less than or equal to 8 or 5 or 2 or 1);

wherein β is an integer that is greater than or equal to 0 and less than or equal to 25 (or less than or equal to 8 or 5 or 2 or 1);

wherein γ is an integer that is greater than or equal to 0 and less than or equal to 25 (or less than or equal to 8 or 5 or 2 or 1);

wherein when D is NR_aR_b , then α optionally is greater than or equal to 1 and less than or equal to 25;

wherein when R_1 , R_m , R_n , R_q , and R_r are each H, and R_o , R_p , and D are each $-\text{CH}_3$, A optionally is not $\text{C}(\text{CN})(\text{CN})$;

wherein when R_1 , R_m , R_n , R_o , and R_p are each H, and R_q , R_r , and D are each $-\text{CH}_3$, A optionally is not $\text{C}(\text{CN})(\text{CN})$;

wherein when R_1 , R_o , R_p , R_q , and R_r are each H, and R_n , R_m , and D are each $-\text{CH}_3$, A optionally is not $\text{C}(\text{CN})(\text{CN})$;

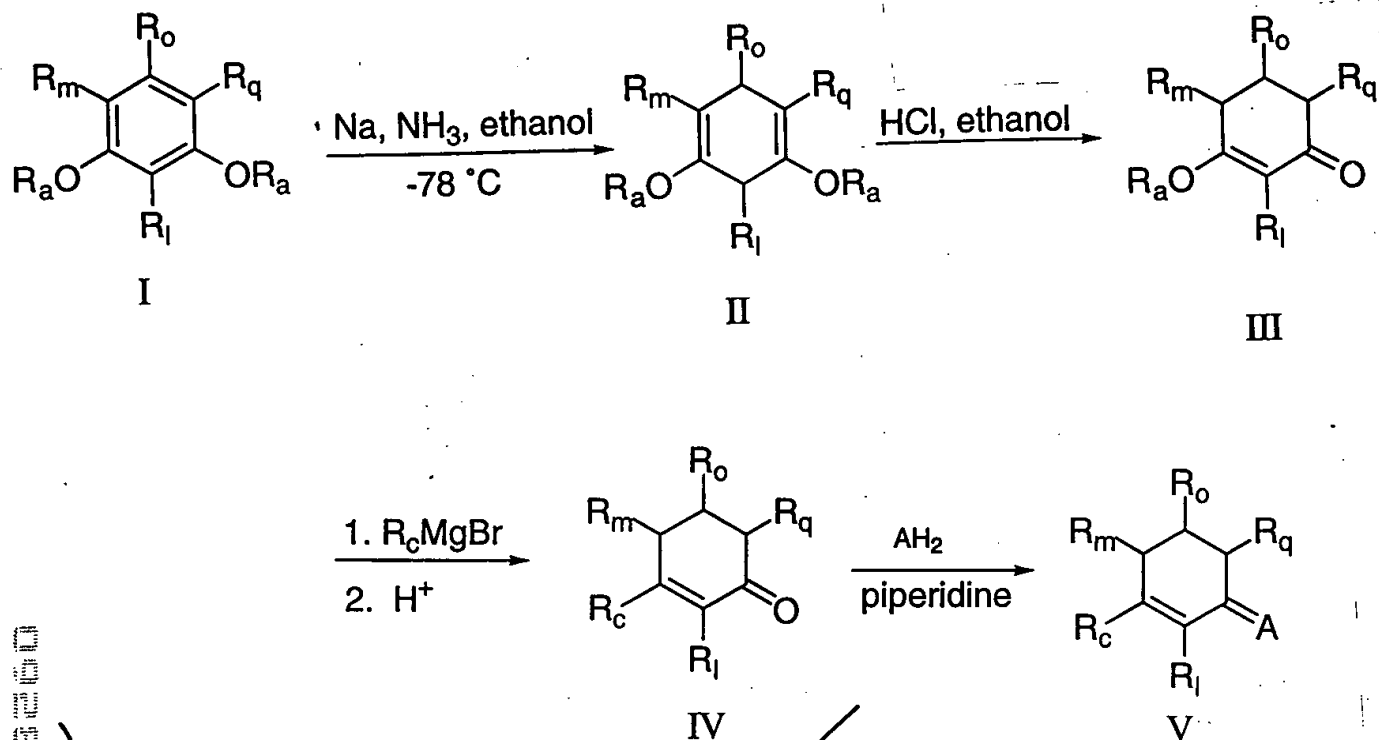
wherein when R_1 , R_m , R_n , R_o , R_p , R_q , and R_r are each H, and D is $-\text{CH}_3$, A optionally is not $\text{C}(\text{CN})(\text{CN})$; and

wherein * represents an attachment point (e.g., the attachment point at which A attaches to X).

In one embodiment, preferably in formula A, R_1 , R_m , R_n , R_o , R_p , R_q , R_r , R_t , R_u , R_v , R_w , and R_x are each H, A is $\text{C}(\text{CN})(\text{CN})$, and D is R_y or OR_y , wherein R_y is selected from the group consisting of a linear alkyl group, a branched alkyl group, and an aryl group.

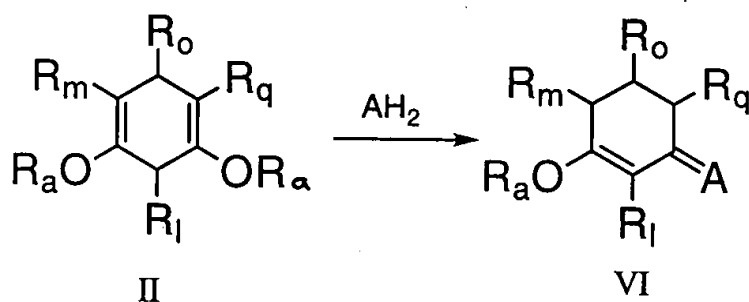
The procedures for making the above-described compounds are set forth below schematically.

Procedure 1:

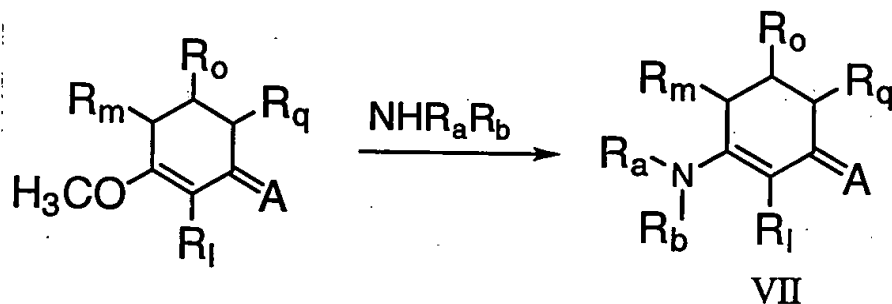


The first step in procedure 1 (i.e., the step that uses compound I to make compound II) is called a Birch reduction. The Birch reduction is described in greater detail in the following two articles, which are incorporated herein by this reference: E. Piers, J.R. Grierson, *J. Org. Chem.*, 1997, 42, 3755-3757; and P. Radlick, *J. Org. Chem.*, 1965, 30, 3209-3211. The last step in procedure 1 (i.e., the step that uses compound IV to make compound V) and below-described procedures 3a, 3b, 3c, and 3d are called Knoevenagel condensation reactions. Knoevenagel condensation reactions are described in greater detail in the following two articles, which are incorporated herein by this reference: R. Lemke, *Synthesis*, 1974, 359-361; and A.J. Fatiadi, *Synthesis*, 1978, 165-204.

Procedure 2a:

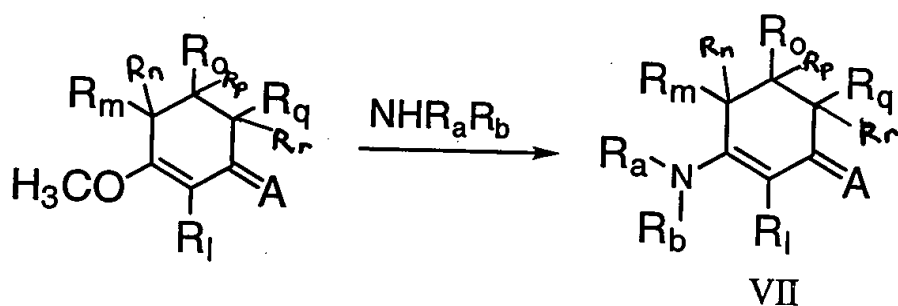


Procedure 2b:



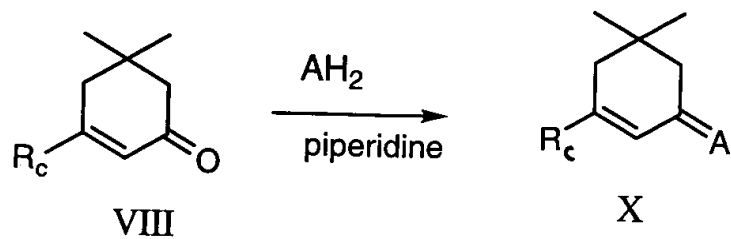
In procedure 2b, R_a and R_b are not both aryl groups.

Procedure 2c:

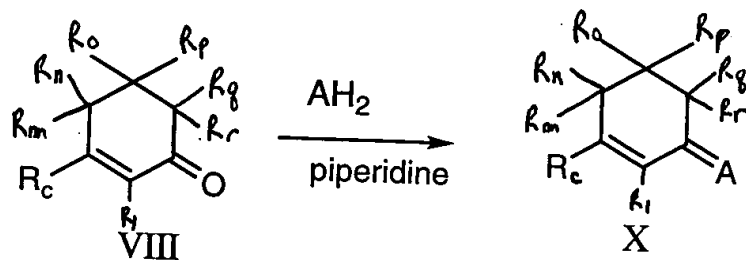


In procedure 2c, R_a and R_b are not both aryl groups.

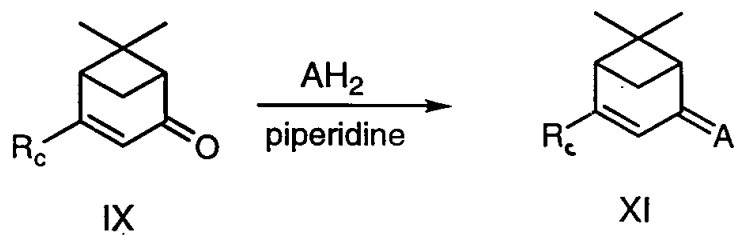
Procedure 3a:



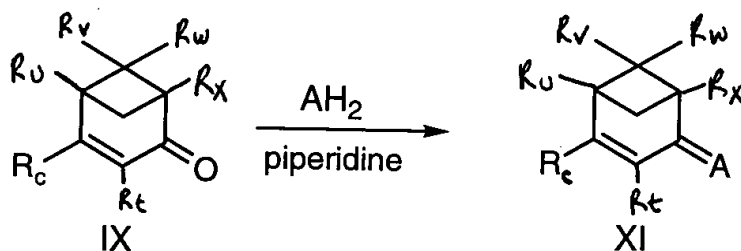
Procedure 3b:



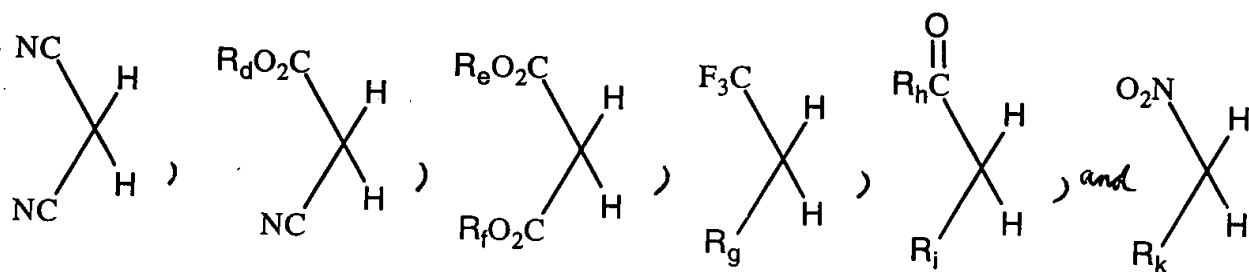
Procedure 3c:



Procedure 3d:

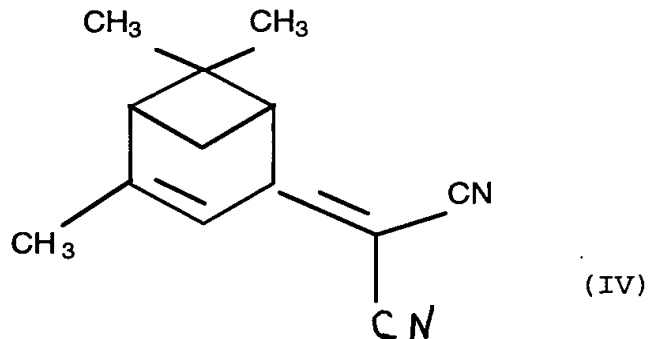
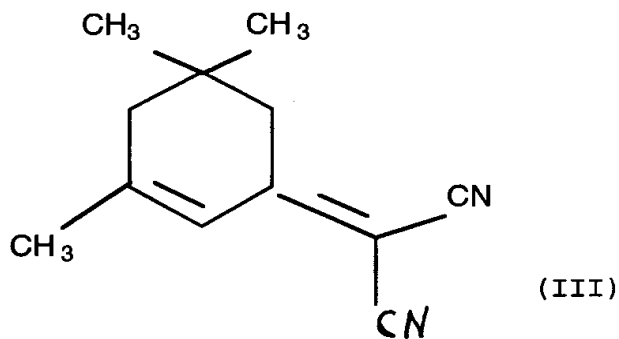
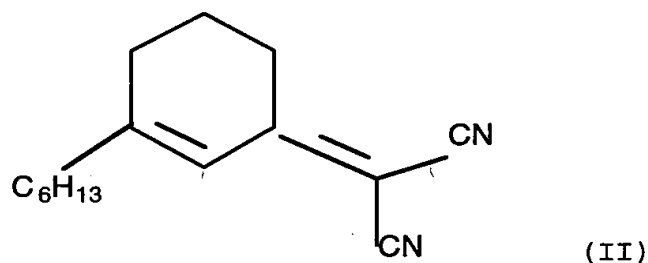
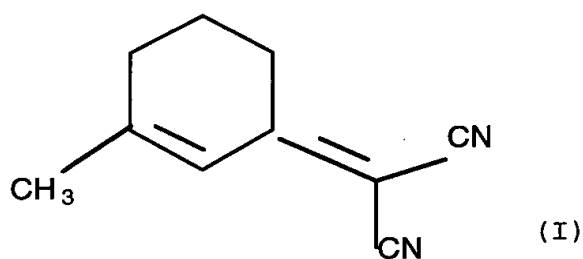


In the procedures described above, AH_2 is selected from the group consisting of:



Compounds wherein D is SR_a may be made by a procedure analogous to procedure 2a above; and compounds wherein D is PR_aR_b may be made by a procedure analogous to procedure 2b above.

Four compounds of the above-described invention were studied. Their molecular structures are shown below in formulas I-IV.



The melting point (in $^{\circ}C$) and heat fusion enthalpy (in kcal/mol) of compounds I-IV are set forth below in Table 1.

Table 1

Compound	Melting Point (in °C)	Heat Fusion Enthalpy (in kcal/mol)
Formula I	84.0	5.93
Formula II	3.4	5.32
Formula III	74.9	6.35
Formula IV	61.2	4.98

There are several reasons for designing these linear polyene molecules. First, these linear polyene molecules exhibit a considerable charge transfer that is confined along the quasi-one-dimensional π -conjugated bridge (i.e., along the bridge comprising two or more unsaturated (e.g., double) bonds). Second, the incorporation of the polyene into a ring-containing bridge prevents isomerization resulting in improved thermal and photochemical stability. Third, the ability to change alkyl groups allows one to control the melting temperature so as to tune the solubility to the LC's. Fourth, the two cyano or cyano/amino groups provide (or more broadly the A group in formula A provides) a huge push-pull effect for enhancing the dipole moment; and fifth, the cyano acceptors themselves have (or more broadly the A group in formula A has) a large group dipole moment.

The threshold voltage, visco-elastic coefficient, and absorption spectra of the compounds of formulas I-III were measured. (The compound of formula IV is a chiral material, so its physical

properties were not studied.) In the sample preparation, we mixed 3% of each compound in a commercial E63™ LC mixture. (E63™ LC mixture is a Merck mixture. Its major components are alkyl cyano-biphenyl and alkoxy cyano-biphenyl. This mixture was used because it has very wide nematic range: its melting point is below -40°C and its clearing point is about 87°C.) These guest-host mixtures were then injected into a homogeneous-aligned cell. The cell gap (i.e., the gap between substrates in a liquid-crystal display) was controlled by spacers to be about 5.6 μm, and the pretilt angle was ~2°. (The pretilt angle is the angle inclined on the liquid crystal substrates. This way, liquid crystals know which way to relax back without creating instability. A typical pretilt angle of an LC cell is 1-5°.) The voltage-dependent phase change method was used for determining the threshold voltage. (The voltage-dependent phase change method has been described in Wu, et al., Phys. Rev. A, 42, 2219-2227 (1990), which is incorporated herein by this reference.) Results measured at λ=633 nm are plotted in Figure 1.

In Figure 1, the axis labelled "Phase Change (π)" is the phase of a liquid crystal cell, wherein the phase is described as $\delta = 2\pi d \Delta n / \lambda$; where d is the cell gap, Δn is the effective birefringence and λ is the wavelength. When a voltage is applied to the liquid crystal cell, the effective birefringence is decreased as the applied voltage is increased. Thus, a phase change 0.5π means $\delta(V=0) - \delta(V) = 2\pi d [\Delta n(V=0) - \Delta n(V)] / \lambda = 0.5\pi$.

In Figure 1, the solid circles represent experimental data of pure E63™ LC mixture; the open circles are for 3% of the compound of formula I dissolved in E63™ LC mixture (i.e., 3% by weight of the total mixture of the compound of formula I and the E63™ LC mixture); the diamonds are for 3% of the compound of formula II dissolved in E63™ LC mixture (i.e., 3% by weight of the total mixture of the compound of formula II and the E63™ LC mixture);

and the triangles are for 3% of the compound of formula III dissolved in E63™ LC mixture (i.e., 3% by weight of the total mixture of the compound of formula III and the E63™ LC mixture).

Results for the compounds of formulas I, II, and III overlap closely due to their similar structures. In the vicinity of threshold voltage, the voltage-dependent phase change is linear. From this linear extrapolation, the threshold voltage is obtained. From Figure 1, the V_{th} of E63™ LC mixture at $f=2$ KHz ($f = 2$ KHz means the frequency of the applied AC voltage) and room temperature (approximately 22°C) is found to be $\sim 1.01 V_{rms}$. Adding 3% by weight of the compounds of formulas I, II and III lowers the threshold voltage to $0.93 V_{rms}$. Knowing that E63™ LC mixture's $\Delta\epsilon$ is 14.6, we estimate that the $\Delta\epsilon$ of the compounds of formulas I, II, and III is extrapolated to be about 50. The observed dielectric anisotropy in the compounds of the present invention is similar to the dielectric anisotropy of the nitro-amino azobenzenes and tolans described in S.T. Wu, et al., Appl. Phys. Lett. 64, 2191 (1994) and Asia Display pp. 567 (1995), and is smaller than the dielectric anisotropy of the bicyano-amino polyenes described in Wu, et al., Jpn. J. Appl. Phys. 37, L1254-56 (1998). However, these previously reported compounds are colored. They have strong absorption in the visible region; and, thus, use of these previously reported compounds is limited.

Increasing dopant concentration would further reduce threshold voltage at the price of increased mixture viscosity. To evaluate the viscosity of these compounds, the decay time was measured for these LC cells with 3% concentrations (by weight) of the compounds

of formulas I, II, and III. Through time-dependent phase change measurements, the visco-elastic coefficients (γ_1/K_{11}) of the guest-host mixtures were determined. (The time-dependent phase change method has been described in Wu, et al., Phys. Rev. A, 42, 2219-2227 (1990).) The measured visco-elastic coefficient (γ_1/K_{11}) for 3% of the compound of formula I dissolved in E63™ LC mixture was 20 ms/ μm^2 ; the measured visco-elastic coefficient (γ_1/K_{11}) for 3% of the compound of formula II dissolved in E63™ LC mixture was 23.8 ms/ μm^2 ; and the measured visco-elastic coefficient (γ_1/K_{11}) for 3% of the compound of formula III dissolved in E63™ LC mixture was 23.7 ms/ μm^2 .

The viscosity of an LC compound is determined by its moment of inertia, molecular shape, and temperature. The compound of formula I has the lowest viscosity as expected from theory because it has the shortest or smallest side chain (i.e., the shortest or smallest D group). (Wu, et al., Jpn. J. Appl. Phys. 37, L1254-56 (1998).) According to this theory, the smaller X group is in formula A, the lower the viscosity and the higher the melting point and the clearing temperature.

The absorption spectra of the compounds of formulas I, II, and III are nearly identical because of the structural similarity of these compounds. To measure absorption, 1% of the compound of formula I (by weight) was dissolved in a UV transparent LC host, ZLI-2359™ LC mixture; and 1% of the compound of formula IV (by weight) was dissolved in another ZLI-2359™ LC mixture. (ZLI-2359™ LC mixture, which is a UV transparent liquid crystal mixture made by Merck, includes some cyclohexane compounds that don't absorb UV light. Thus, ZLI-2359™ LC mixture is a good host for UV absorption measurements.) A homogeneous cell with an approximately 6- μm cell gap was used for measurements. The results are shown in Figure 2, wherein "a.u." represents arbitrary units. Figure 2 shows that

the compounds of formula I and IV are highly transparent throughout the entire visible spectral region.

The clearing temperature (T_c) of such a guest-host system is reduced much faster than the linear extrapolation from a eutectic mixture: $(T_c)_{gh} = x(T_c)_g + (1-x)(T_c)_h$, wherein x is the concentration of the dopant/guest, "g" refers to the guest, and "h" refers to the host. The host mixture E63™ LC mixture's clearing-point temperature is ~87°C. When 3% of the compound of formula II is added to the host, the extrapolated clearing-point temperature (T_c) should be ~84.5°C, according to the formula set forth in the first sentence of this paragraph. However, the measured T_c was ~65°C. This indicates that the compound of formula II causes a larger-than-expected molecular separation. This is evidenced by the fact that the mixture birefringence drops from 0.22 for pure E63™ LC mixture to 0.21 and K_{11} drops from 12.6 to 11.2 pico-Newton after 3% of the compound of formula II is added to the E63™ LC mixture.

A high clearing point (e.g., about 70-100°C) is normally preferred, but in some circumstances, a low clearing point finds interesting applications as well. For example, for nonlinear optical effects using isotropic LC's, it is important to have an LC mixture with an isotropic phase (i.e., a phase with no visible crystals) below room temperature. (The isotropic phase is the phase at which the liquid-crystalline behaviors disappear. As the temperature goes beyond the clearing temperature, the liquid crystal becomes an isotropic liquid. That means many or all the anisotropic behaviors, such as optical and dielectric anisotropy, disappear.) The light scattering of an LC at the isotropic state is 2-3 orders of magnitude lower than that in the nematic state. (S.T. Wu and K.C. Lim, Appl. Opt. 26, 1722-1727 (1987).) (The nematic state means the temperature range in which the nematic phase exists.

Liquid crystal exists in only a certain temperature range. The sequence of phase transition is: crystalline phase, nematic phase, and isotropic phase.)

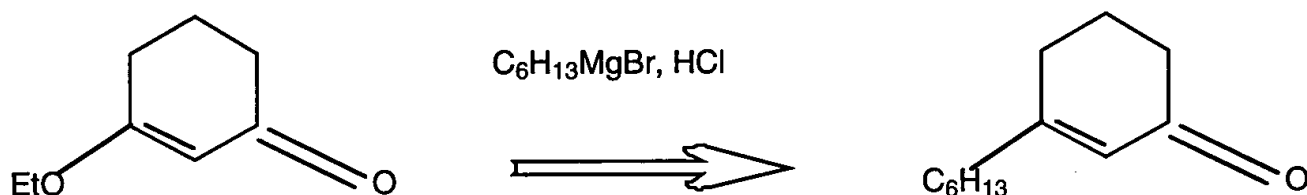
Another potential application of this tunable T_c is to control the mixture with large temperature-dependent refractive indices, $\partial n/\partial T$. It is well-known that $\partial n/\partial T$ is much enhanced when the temperature is about 2-3 degrees Centigrade below T_c . (I.C. Khoo and S.T. Wu, Optics and Nonlinear Optics of Liquid Crystals (World Scientific, Singapore, 1993)) For example, to operate a liquid crystal device at room temperature (e.g., 22°C), then one must design a liquid-crystal mixture with a clearing point about 2-5 degrees Centigrade above room temperature in order to take advantage of a large $\partial n/\partial T$.

Figure 3 shows the concentration-dependent clearing temperature (left) and birefringence (right) of a Merck E7™ liquid-crystal mixture. The compound of formula II was used as the guest dopant; and an E7™ LC mixture was used as the host. The major component of an E7™ LC mixture is cyano-biphenyl. The melting point of the E7™ LC mixture is about 59.5°C; and Δn is about 0.224 at room temperature (about 22°C) and $\lambda=633\text{nm}$. As the guest concentration increased, both the clearing point and birefringence decreased almost linearly. At about 10% concentration by weight (i.e., when the guest comprised about 10% by weight of the guest-host mixture), the guest-host mixture's clearing point dropped to about 28°C; and birefringence dropped to about 0.135. The decreased birefringence is partly related to the decreased clearing point. At a low clearing point, the corresponding order parameter of the mixture at room temperature is reduced. On the other hand, at 10% concentration, the guest-host mixture's melting temperature was suppressed to about -30°C. Thus, the 10% guest-host mixture not only had a large $\partial n/\partial T$ (the rate of refractive index change) at room temperature (about 22°C), but also had a low melting

temperature for practical applications.

The compounds of formulas I, II, III, and IV were made by a Knoevenagel reaction between ketones and malononitrile with a few drops of piperidine. Details regarding procedures 1, 2a, 2b, 2c, 3a, 3b, 3c, and 3d, which are described above, can be found in the following preparation procedures.

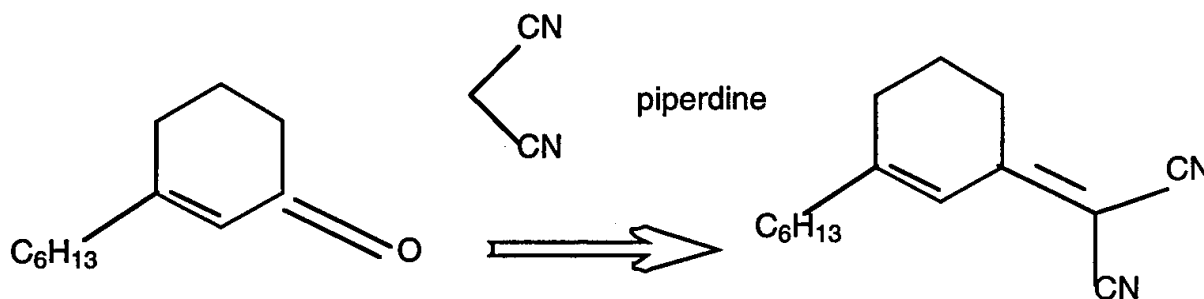
Preliminary step: Preparing 3-Hexyl-2-cyclohexenone



To a solution of 3-ethoxy-2-cyclohexenone (8.62 g, 61.50 mmol) in dry THF (tetrahydrofuran), hexylmagnesium bromide (15.38 mL, 2.0 M, 30.75 mmol) was added dropwise with stirring. The mixture was kept at 0°C (in an ice-water bath) during the whole process and then was allowed to warm (the ice-water bath was removed) to ambient temperature (approximately 22°C). Hydrochloric acid (10 mL, 3.0 M) was added to the above mixture. The mixture was extracted with diethylether 3 times. The combined organic layers were washed with water and then dried over magnesium sulfate. The product was further purified by flash chromatography on silica gel using 10:100 (dichloromethane:hexane (volume:volume)) to yield 6.17 g (xx%) of 3-hexyl-2-cyclohexenone. ^1H NMR (300 MHz, CDCl_3): δ 5.78 (s, 1 H), 2.40-2.20 (m, 4 H), 2.20-2.10 (t, $J = 7.37$ Hz, 2H), 1.90 (p, $J = 6.50$ Hz, 2 H), 1.42 (t, $J = 7.30$ Hz, 2 H), 1.22 (br, 6 H), 0.81 (t, $J = 6.70$ Hz, 3 H). ^{13}C NMR (75 MHz,

CDCl₃): 200.06, 167.00, 126.04, 38.49, 37.80, 32.02, 30.11, 29.35, 27.35, 23.21, 22.95, 14.42, GC/MS calculated for C₁₂H₂₀O 180.15, found 180.15. The foregoing gas chromatography/mass spectrometry measurements confirmed the structure.

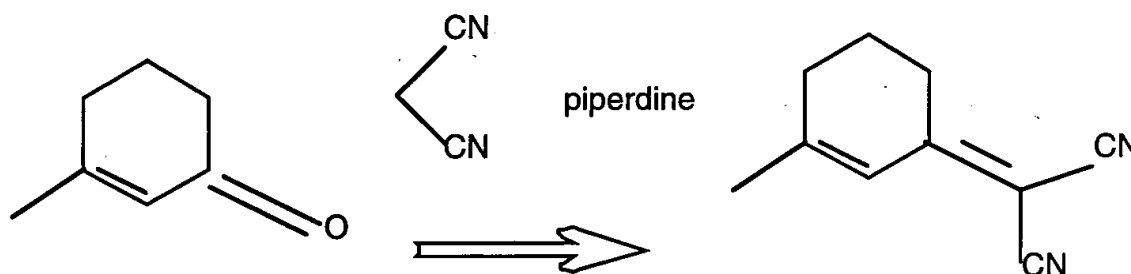
Preparing the compound of formula II



3-Hexyl-2-cyclohexenone (6.17 g, 34.22 mmol) and malononitrile (6.78 g, 102.63 mmol) and piperidine (2 drops (i.e. approximately 0.2 ml)) were stirred overnight (approximately 12 hours). The mixture was purified by flash chromatography on silica gel using 10:100 (dichloromethane:hexane (volume:volume)) to yield the compound of formula II (6.62 g (85%)). ¹H NMR (300 MHz, CDCl₃): δ 6.57 (s, 1 H), 2.71 (t, J = 6.31 Hz, 2 H), 2.31 (m, 4 H), 1.86 (p, J = 6.12 Hz, 2 H), 1.51 (t, J = 7.31 Hz, 2 H), 1.29 (br, 6 H), 0.88 (t, J = 6.60 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃): 171.32, 167.03, 121.27, 121.08, 113.71, 112.97, 39.60, 32.03, 30.43, 29.87, 29.49, 27.83, 23.00, 22.11, 14.51. HRMS (high resolution mass spectrometry) calculated for C₁₅H₂₀N₂ 228.1626, found 228.1617. Elemental analysis calculated for C₁₅H₂₀N₂; C, 78.90; H, 8.82; N,

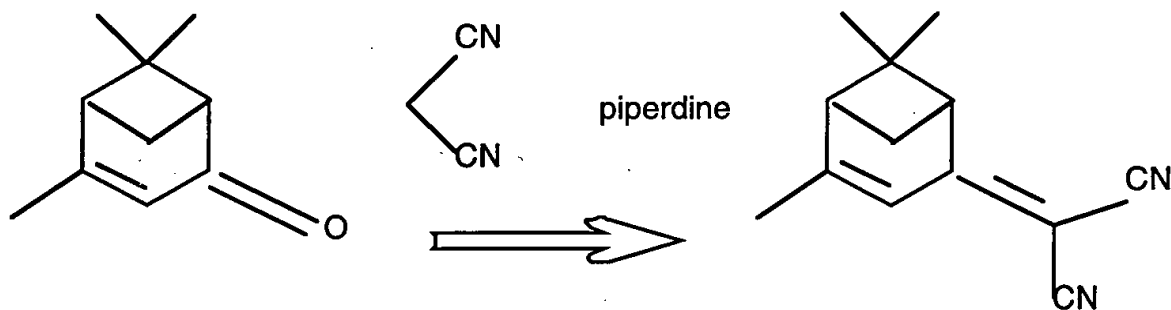
12.26. Found: C, 78.94; H, 8.87; N, 12.20. UV-Vis in CH_2Cl_2
 $\lambda_{\text{max}} = 305 \text{ nm}$. The foregoing data confirm the final product.

Preparing the compound of formula I



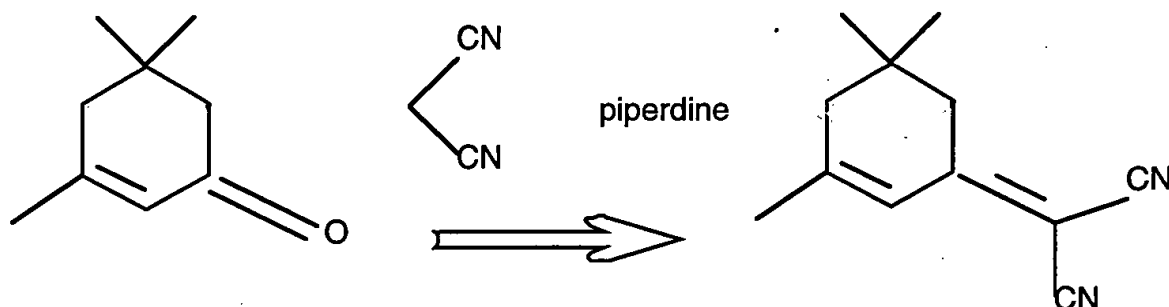
3-Methyl-2-cyclohexen-1-one (2.0 g, 18.16 mmol), malononitrile (3.60 g, 54.47 mmol) and piperidine (3 drops (i.e., approximately 0.2 or 0.3 ml) were heated to 80°C overnight (approximately 12 hours). The product was purified by flash chromatography with hexane:acetone (10:1 (volume:volume)) on silica gel to give 1.78 g (62%) of the compound of formula I. ^1H NMR (300 MHz, CDCl_3): δ 6.63 (s, 1 H), 2.71 (t, $J = 6.50 \text{ Hz}$, 2 H), 2.35 (t, $J = 5.78 \text{ Hz}$, 2 H), 2.08 (s, 3 H), 1.90 (p, $J = 6.34 \text{ Hz}$, 2 H). ^{13}C NMR (75 MHz, CDCl_3): 171.20, 162.47, 122.18, 121.08, 113.68, 112.92, 31.85, 29.57, 25.84, 21.96. Anal. calculated for $\text{C}_{10}\text{H}_{10}\text{N}_2$; C, 75.92; H, 6.37; N, 17.70. Found: C, 75.80; H, 6.42; N, 17.85. UV-Vis in CH_2Cl_2 $\lambda_{\text{max}} = 305 \text{ nm}$. The foregoing data for NMR, elemental analysis, and the compound's UV-Vis spectrometry confirm the structural identity of the final product.

Preparing the compound of formula IV



(1S)-(-)-Verbenone (7.89 g, 52.50 mmol), malononitrile (10.05 g, 157.50 mmol), and piperidine (0.29 mL) were heated to 80°C overnight (approximately 12 hours). The product was purified by flash chromatography with hexane:acetone (10:1) on silica gel to give 7.49 g (72%) of the compound of formula IV. ^1H NMR (300 MHz, CDCl_3): δ 6.48 (s, 1 H), 3.33 (t, J = 5.55 Hz, 1 H), 2.83 (q, J = 5.40 Hz, 1 H), 2.49 (t, J = 5.53 Hz, 1 H), 2.10 (s, 3 H), 1.92 (d, J = 9.29 Hz, 1 H), 1.57 (s, 3 H), 0.93 (s, 3 H). HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2$ 199.1235, found 199.1232. Anal. calculated for $\text{C}_{13}\text{H}_{15}\text{N}_2$; C, 78.75; H, 7.11; N, 14.12. Found: C, 78.79; H, 7.09; N, 14.15. UV-Vis in CH_2Cl_2 λ_{max} = 320 nm. The foregoing data for NMR, elemental analysis, and the compound's UV-Vis spectrometry confirm the structural identity of the final product.

Preparing the compound of formula III



The compound of formula III was synthesized in the same manner as described above for the compound of formula I. Isophorone (7.25 g, 52.46 mmol), malononitrile (10.05 g, 157.50 mmol), piperidine (0.29 mL) were heated to 80°C overnight (approximately 12 hours). The product was purified by flash chromatography with hexane:acetone (10:1) on silica gel to give 6.89 g (73%) of the compound of formula III. ¹H NMR (300 MHz, CDCl₃): δ 6.63 (s, 1 H), 2.53 (s, 2 H), 2.20 (s, 2 H), 2.05 (s, 3 H), 1.03 (s, 6 H). ¹³C NMR (75 MHz, CDCl₃): 170.88, 160.37, 121.07, 113.70, 112.92, 46.21, 43.18, 32.88, 28.33, 25.79. HRMS calculated for C₁₂H₁₄N₂ 185.1157, found 186.1150. Anal. calculated for C₁₂H₁₄N₂: C, 77.38; H, 7.57; N, 15.03. Found: C, 77.35; H, 7.59; N, 15.04. UV-Vis in CH₂Cl₂ λ_{max} = 304 nm. The foregoing data for NMR, elemental analysis, and the compound's UV-Vis spectrometry confirm the structural identity of the final product.

All of the measurements set forth in this application are approximations.

The invention illustratively disclosed herein suitably may be practiced in the absence of any element which is not specifically disclosed herein.

The following claims are entitled to the broadest possible scope consistent with this application. The claims shall not necessarily be limited to the preferred embodiments or to the embodiments shown in the examples.